Off–Shelf Fluxes of Labile Materials by an Upwelling Filament in the NW Iberian Upwelling System

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Abstract

Daily changes on the concentration of carbon and nitrogen species were monitored during the course of a lagrangian drifter experiment in a recurrent upwelling filament south of Cape Finisterre (NW Iberian Upwelling System). The drifting buoy was released at the southern edge of the upwelling centre generated by the Cape and displaced 60 km south–west from 3 to 7 August 1998. Organic matter in the 50m deep study water mass (average 77±2 µM–C) consisted of: **1**) 57 µM–C of dissolved organic matter (DOM) with a C/N molar ratio of 19±2; **2**) 6 µM–C of DOM with a C/N ratio of 9±2; and **3**) 14 µM–C of 50% DOM and 50% suspended organic matter (POM_{susp}) with a C/N ratio of 6.0±0.4. Net conversion of consumed inorganic salts into accumulated TOM = POM_{susp}+DOM was ~40% for nitrogen and ~30% for carbon. Since the study water parcel crosses the shelf–edge, these conversion efficiencies are equivalent to net horizontal export–ratio of 0.4 and 0.3 respectively. A second drifter was deployed in the offshore–end of the filament, and displaced 20 km west from 14 to 17 August 1998. Nitrate was exhausted in the study water mass and no significant changes were observed in the measured variables during the course of the second experiment. Low C/N ratios (6.5±0.4) and rapid POM_{susp}/DOM inter–conversion in the 20 µM–C excess observed in the study volume points to the persistence of the labile materials formed on the shelf during transport to the ocean. Our numbers demonstrate the **1**) key role of upwelling filaments in off–shelf export of organic materials and **2**) the major contribution of DOM to this horizontal export, a previously unaccounted amount. The high nitrogen content of the exported materials makes it an attractive organic substrate for use by microbial populations in the adjacent oligotrophic ocean.

Keywords: DOM, POM, filaments, coastal upwelling, NW Iberian margin

Contents

1. Introduction

Ocean margins are pre–eminent sites for phytoplankton net primary production in response to enhanced nutrient fluxes from adjacent continental and ocean waters. Despite ocean margins cover only 8% of the total ocean surface, they support 18–33% of the global net primary production and 27–50% of the global export production, according to different estimates (Walsh, 1991; Chavez & Toggweiler, 1995; Wollast, 1998). Considerations on the fate of exported materials have centred on sinking particulate organic matter (POM_{sink}), sedimented on the shelf (Falkowski, Flagg, Rowe, Smith, Whitledge & Wirick, 1988; Biscaye, Flagg & Falkowski, 1994) or transported offshore and deposited on the slope (Walsh, Rowe, Iverson & McRoy, 1981). Despite the recognised relevance of fresh suspended (POM_{susp}) and dissolved (DOM) organic matter to marine carbon cycling (eg. Kirchman, Lancelot, Fasham, Legendre, Radach, & Scott, 1993; Hansell & Carlson, 1998), its contribution to the export production of ocean margins has not been quantified yet (Wollast, 1998).

Ocean margins affected by wind–driven upwelling reacts to magnified nutrient inputs from the ocean by enhancing organic matter production, recycling and export (Walsh, 1991). Horizontal offshore transport of the export production is favoured there, specially at sites where large upwelling filaments develop (e.g. Brink & Cowles, 1991; Gabric, García, Camp, Nykjaer, Eifler, & Schrimpf, 1993; Barton et al., 1998). However, even recent modelling approaches to horizontal carbon export by upwelling filaments (Gabric, Eifler, & Schrimpf, 1996; Moisan, Hofmann, & Haidvogel, 1996) have neglected the key contribution of fresh DOM.

Recent works in the NW Iberian upwelling system confirm the major contribution of DOM to the excess of phytogenic materials accumulated in shelf surface waters south of Cape Finisterre (Álvarez–Salgado, Doval & Pérez, 1999). A large filament is regularly observed at that position (Haynes, Barton & Pilling, 1993). The westward extension of this filament depends on the intensity of the recurrent upwelling episodes (~2 wk period; Álvarez–Salgado, Rosón, Pérez & Pazos, 1993) during the April–May to September–October upwelling season at our latitudes, 42°–43°N (Wooster, Bakun & McClain, 1976). The aim of the present work is to

study the short–time–scale evolution of the dissolved and suspended, organic and inorganic, carbon and nitrogen stocks in a parcel of recently upwelled Eastern North Atlantic Central Water (ENACW), which subsequently moved offshore following the upwelling filament recurrently observed south of Cape Finisterre. The net ecosystem metabolism (NEM) of carbon and nitrogen species in the study water parcel, *i.e*. the net balance of the production minus the respiration of autotrophs and all heterotrophs there, will be inferred. A realistic estimation of the horizontal export ratio (e–ratio) of organic materials across the shelf–edge, *i.e*. the fraction of the NEM in the upwelling centre off Cape Finisterre that is exported to the adjacent ocean, will be performed. Although horizontal export of dissolved organic matter have been recently considered to estimate the e–ratio of the oceanic equatorial upwelling (e.g. Archer, Peltzer & Kirchman, 1997), it is accounted for the first time in any study of ocean margins. Finally, the simultaneous determination of carbon and nitrogen stocks will allow discussion on the key issue of the lability of the exported materials, as derived from the study of the C/N ratios.

2. Materials and Methods

2.1. The Lagrangian study

Upwelling filaments off the western Iberian Peninsula become common in early July, reach maximum offshore extension in late September and are rare in late October, after the onset of the poleward–flowing slope current of warm subtropical water characteristic of the downwelling season at our latitudes (Haynes et al., 1993). The study filament is observed south of Cape Finisterre during the upwelling season and it is the longest one off the western Iberian Peninsula, both in terms of mean (150–170 km) and maximum (245–280 km) lengths. It is probably originated by topographic forcing and shelf induced wind–stress variation in the area, where the 'Rías Baixas' channel the wind to the south–west.

Rapid offshore advection of shelf surface waters carried by an upwelling filament has been observed by direct current measurements and by drifter trajectories (Brink & Cowles, 1991; Haynes et al., 1993). Entrainment and subsequent offshore transport of recently upwelled water near the coast occurs in parallel to filament development (Moissan & Hoffman, 1996).

Lagrangian drifters have been throughoutly used to track water masses, allowing the construction of budgets with the assumption of reduced vertical and horizontal advection within the volume under investigation (e.g. Moisan & Hoffman, 1996). In this study, a surface drifting buoy with suspended sediment traps was used to track the study water parcel. Discrete samples were taken daily at ~02:00, ~09:00 and ~12:00 GMT from 6–8 depths throughout the upper 150m (see Fig. 1 for 02:00 GMT stations position). The buoy was first released at the southern edge of Cape Finisterre upwelling centre and drifted southwards from 3 to 7 August, crossing the shelf–edge. On 14 August, a second drifter was deployed in the core filament, and moved south–westwards until 17 August. During the filament study additional seawater samples from 500m depth were taken at selected stations to have reference values of the chemical characteristics of waters below ENACW. A detailed description of the two drifter studies ––with a rational validation of their Lagrangian nature and the consistency of the temporal sequence from the coastal to the filament study–– can be found in Joint, Inall, Torres–Almarza, Figueiras, Álvarez–Salgado and Woodward (this issue).

2.2. CO_2 system, nutrients, dissolved oxygen, chlorophyll and microplankton determinations

The measurement of pH was made using a Ross combination electrode (ORION) calibrated on the Total Hydrogen Ion Concentration Scale ($mol \cdot kgSWS^{-1}$) with the TRIS and AMP buffers according to Dickson (1993). Total Alkalinity (TA) was measured using classical Gran electrotitration. TA calculation was made with corrections for fluoride and sulfate according to Hansson and Jagner (1973). Total Inorganic Carbon (C_T) computations were made with the dissociation constants of carbonic acid from Roy et al. (1993) and the dissociation constant of HSO_4^- from Dickson (1990). C_T and TA have been normalised to salinity 35.0 to produce the corresponding NC_T and NTA parameters, which depend only on the biological and geochemical activity in the study water parcel. The contribution of $CaCO_3$ fixation ––not related to NO_3^- consumption and O_2 production–– has to be subtracted from NC_T. For systems where NO_3^- is the dominant inorganic nitrogen species, as in the present study, the $CaCO_3$–corrected NC_T (NC_Tcor) can be calculated as (Broecker & Peng, 1982):

$$NC_Tcor = NC_T - 0.5 \cdot (NTA + NO_3^-)$$

Analyses of dissolved nutrient concentrations were performed just after sampling. Water samples were carefully transferred from the rosette sampler to clean Nalgene bottles, every effort being made to reduce contamination. Nutrient concentrations were measured by colorimetric autoanalysis in a Technicon segmented flow colorimetric autoanalyser. Nitrate was measured using the method of Brewer and Riley (1965), nitrite by the procedure of Grasshoff (1976), silicate and phosphate by the methods of Kirkwood (1989), and ammonia by the method of Mantoura and Woodward (1983).

In addition, low concentrations (<50 nM–N) of nitrate and ammonium were also measured using sensitive analytical procedures. Nitrate and nitrite concentrations were determined by the chemiluminescence method of Garside (1982) and low nanomolar concentrations of ammonia were measured by the fluorescence analytical method of Jones (1991). Dissolved oxygen was measured by the Winkler method using a potentiometric end–point determination. Apparent oxygen utilization, AOU= O_2sat–O_2, is calculated using Benson and Krause´s equation (UNESCO, 1986) for oxygen saturation (O_2sat).

Chlorophyll concentrations were measured by spectrophotometric (Parsons, Maita & Lalli, 1984) and fluorometric (Holm–Hansen, Lorenzen, Holmes, & Strickland, 1965) analysis of extracted pigments. 1–2 L aliquots of water from the above experiments were filtered through Whatman GF/F filters for spectrophotometric analysis, or 100ml samples were filtered through polycarbonate filters for fluorometric determination of chlorophyll concentration in three size fractions (>5µm, <5 to >2µm and <2µm); all filters were frozen until return to the laboratory. Pigments were extracted by addition of 90% acetone and stored in the dark at 4°C for ca 12h prior to analysis.

Samples for microplankton counts were preserved in Lugol's iodine and sedimented in 100ml composite chambers. Diatoms, dinoflagellates, flagellates and ciliates were identified and counted using an inverted microscope. Cell numbers were converted into carbon biomass as described by Joint et al. (this issue).

2.3. Dissolved and suspended organic matter measurements

DOM (∅< 0.8 μ) and POM_{susp} (0.8 μ< ∅ <200 μ) concentrations in the water column were determined during the course of the experiment. Seawater for the analysis of POM_{susp} was drawn from the Niskin bottles in 2 litre polycarbonate flasks. It was immediately filtered with an oil–less vacuum filtration system (filtration pressure <0.3 kg cm^{-2}) to collect the suspended material in 25 mm ∅ Whatman GF/F filters (precombusted 450 °C, 4 hours). The filters were dried on silica gel and frozen to –20ºC until analysis in the laboratory. Suspended organic carbon (POC_{susp}) and nitrogen (PON_{susp}) measurements were carried out with a 'Perkin Elmer 2400 CHN' analyser. Catalytic combustion of POC_{susp} and PON_{susp} to CO_2 and NO_X respectively was performed at 900ºC and reduction of NO_X to N_2 at 640ºC. Acetanilide was used to calibrate the system. The analytical error of the method is ±0.1 μM–C for POC_{susp} and ±0.04 μM–N for PON_{susp}.

Samples for the analyses of dissolved organic matter (DOM) were collected into 250 ml acid–cleaned all–glass flasks. They were immediately filtered through 47 mm ∅ Whatman GF/F filters (precombusted 450°C, 4 hours) in an acid–cleaned all–glass filtration system, and collected in 10 ml glass ampoules (precombusted 450°C, 12 hours). After acidification with H_3PO_4 to pH <2, the ampoules were heat–sealed and preserved in the dark at 4°C, until analysed in the laboratory. A nitrogen specific 'Antek 7020' nitric oxide (NO•) chemiluminescence detector was coupled in–series with the carbon specific Infra–Red Gas Analyser (IRGA) of a 'Shimadzu TOC–5000' organic carbon analyser, in conjunction with a PC–based integration software package ('Integrador v1.2', Fractal Info, Spain) as described in Álvarez–Salgado and Miller (1998). An injection cycle took ~4 min. As each sample was injected 3–4 times, ~12–16 min were necessary for completion. The system was standardised daily with a mixture of potassium hydrogen phthalate and glycine. The system blank ––obtained by frequent injection (every 4–6 samples) of UV–Milli–Q water–– was equivalent to 10 μM–C and 0.4 μM–N. Precision of both simultaneous measurements was about ±1 μM–C and ±0.3 μM–N. The accuracy of our DOC measurements were tested daily with the reference materials provided J.

Sharp (University of Delaware) with very satisfactory results. We obtained an average concentration of 45.1±0.7 μM–C (n= 52) for the DEEP OCEAN reference (Sargasso Sea deep water, 2600 m) and 0.4±0.6 μM–C (n= 52) for the BLANK reference material. The nominal values provided by the reference laboratories are 44.0 ±1.5 and 0.0±1.5 μM–C respectively.

Dissolved organic nitrogen (DON) concentration in the samples can be obtained by subtracting the independently measured NO_3^- to the HTCO–TDN. A problem with the precision of DON measurements remains in NO_3^- rich upwelled waters, where the DON contribution to the TDN signal is small (~3.5 μM–N DON from ~12 μM–N TDN). The standard deviation of the DON concentration can be calculated as $\sigma_{DON} = \sqrt{\sigma_{TDN}^{\ 2} + \sigma_{DIN}^{\ 2}}$. Since the analytical error of NO_3^- measurements is ±0.1 μM–N, the precision of DON estimation for upwelled waters would be ~10% or ±0.3 μM–N.

3. Results

3.1. The coastal upwelling study

Nitrogen species (NO_3^-+NO_2^-, DON and TON = PON_{susp}+DON) have been chosen to present the time evolution of the chemical setting during the lagrangian experiment (Fig. 2). A DON & TON excess and NO_3^-+NO_2^- (hereinafter NO_3^-) deficit is observed in the study water parcel (shaded area in Fig. 2) compared with levels recorded in the cold and nutrient–rich upwelled ENACW below: ~3.7 μM–N TON and ~7.5 μM–N NO_3^- at 150 m depth respectively. NO_3^- stocks reduce dramatically from 3 to 7 August, which is met with a concomitant DON & TON accumulation. Average NO_3^- concentration in the study volume decreases from ~3 μM–N to <0.4 μM–N (Fig. 3a), most of the consumption occurring during 3 August at a rate of ~2 μM–N d^{-1}. No changes of NH_4^+ concentrations (not shown) are observed during the course of the experiment. Net inorganic carbon (NC_Tcor) consumption and oxygen production (c.f. AOU) follow the NO_3^- trend (Fig. 3b). The NC_Tcor/NO_3^- molar ratio is 9±2 and indicates production of organic matter with carbohydrate excess if compared with the Redfield composition of planktonic organic matter, which has a C/N ratio of 6.7 (Anderson, 1995). Accumulation of

PON_{susp} and DON accompany NO_3^- consumption (Fig. 3a). PON_{susp} peaks on 4 August whilst a brief DON maximum is recorded one day later, suggesting partial conversion of recently formed PON_{susp} into DON. The efficiency of the system to convert NO_3^- into TON is ~40% when the whole inshore–start study period is considered. Figure 4a shows the conspicuous time evolution of the C/N molar ratio of POM_{susp} and DOM transported by the study water parcel. C/N ratios are high in recently upwelled ENACW of the upwelling centre and decreased at stations with POM_{susp} and DOM maxima, indicating increased contribution of N–rich labile material. Subsequent increase in C/N ratios suggests partial consumption of N–rich material. The evolution of chlorophyll concentrations in the study water parcel (average 1.2±0.2 mg Chl m^{-3}; Fig. 4b) is parallel to the PON_{susp} trend (Fig. 3a) and denotes a progressive increase of the >5 µm fraction (average 43% of the total). Accordingly, diatoms represent <2% of the total microplankton carbon on 3 August and increase to 24% on 7 August (Fig. 4c). Dinoflagellates are the most abundant microplankton group. They represent 67% of the total microplankton carbon form 3 to 7 August.

Results arising from Figures 3 and 4 are reinforced by the analysis of the correlation between measured chemical parameters presented in Figure 5. All the individual samples from the surface to 150 m at the 3 daily sampling times have been considered. It must be noticed that the contribution of continental runoff to surface waters is negligible during the experiment. Average salinity in the study volume was 35.68±0.02, which represents <0.4% of freshwater compared with the salinity of upwelled ENACW (<35.80). This is the expected behaviour from the climate conditions in the study area. Average August 1987–96 continental runoff and offshore Ekman transport off the 'Rías Baixas' was 25 L s^{-1} km^{-2} of drainage basin and 385 m^3 s^{-1} km^{-1} of coast (Nogueira, Pérez & Ríos, 1997). Considering a total drainage basin of 6800 km^2 and a coast 110 km long, 99.6% of surface waters on the shelf came from the adjacent ocean mediated through upwelling. Consequently, the origin intercept and slope of the correlations presented in Figure 5 indicate the chemical transformations operated in the oceanic ENACW which enters the shelf and upwells to the outgoing photic layer, where the production, recycling

and export of phytogenic materials occurs. This kind of approach have been successfully applied by Hansell and Carlson (1998) to study the NEM of the Equatorial Pacific and other marine systems.

Spatial and temporal NC_Tcor and NO_3^- changes are extremely coupled throughout the water column (r = +0.95). The NC_Tcor/NO_3^- slope of 7.7±0.3 mol C mol N^{-1} (Fig. 5a) is comparable with the value of 9±2 mol C mol N^{-1} obtained from the time changes in the study water parcel (Fig. 3b). Changes in the TOC and TON pools (Fig. 5b) are also well correlated (r= + 0.88) with a TOC/TON slope of 6.0±0.4 mol C mol N^{-1}, *i.e.* about 23% lower than the stoichiometric ratio of net nutrient utilisation (7.7±0.3 mol C mol N^{-1}). The direct correlation of POC_{susp} and PON_{susp} is very good as well (r= +0.96), with a slope of 5.9±0.2 mol C mol N^{-1} (Fig. 5c), the same than for the total organic material. Consequently, the fraction of DOM that forms simultaneously with POM_{susp} has about the same C/N ratio and could be considered as labile as POM_{susp}. This labile faction of DOM can be obtained from the linear regressions between TOC/POC_{susp} (r= +0.89; Fig. 5d) and TON/PON_{susp} (r= +0.92; Fig. 5e). The slopes TOC/POC_{susp} = TON/PON_{susp} = 1.9±0.1 indicate that the fraction of DOM formed at the same time–scale than POM_{susp} is of about the same magnitude than POM_{susp}. The origin intercept of these regressions (63±1 µM–C and 3.7±0.1 µM–N) represents the constant amount of DOC and DON in POM–free upwelled water. The C/N molar ratio of this dissolved material, 17±1, is about 3–fold the ratio of the labile material. These numbers agrees very well with the DOC and DON concentrations found by Álvarez–Salgado et al. (1999) in recently upwelled ENACW in the same study area. The labile fraction of DOC and DON only represents 8% and 19% of the average DOC and DON concentrations in the water column. DOC and DON in upwelled ENACW (150 depth) is ~10% and ~20% above the constant concentration of 57±1 µM–C and 3.0±0.3 µM–N observed at 500 m depth (not shown). The C/N molar ratio of DOM at 500 m increases to ~19±2, pointing the refractory nature of this material.

An inverse linear correlation (r = –0.86) is observed between TON and NO_3^- (Fig. 5f). The TON/NO_3^- slope of –0.43±0.03 is comparable with the value of 0.4 obtained from the time

changes in the study water parcel (Fig. 3a). It indicates that the conversion efficiency of 40% is applicable both at the time–scale of the study volume (~1 wk) and the time–scale of the flushing time of upwelled ENACW on the shelf during upwelling episodes (~4 wk). The late number has been obtained considering a volume of ~250 km^3 for shelf waters off the 'Rías Baixas', an offshore Ekman transport of 1000 m^3 s^{-1} (km of coast)$^{-1}$ during upwelling episodes (Álvarez–Salgado et al., 1993) and a coast ~110 km long. An inverse linear correlation (r= –0.85) is also observed between TOC and NC_Tcor (not shown), with a resultant TOC/NC_Tcor slope of –0.29±0.03. Consequently, the conversion efficiency reduces to 0.3 for the case of carbon. Considering the TOC/NC_Tcor, TON/NO_3^-, TOC/TON and NC_Tcor/NO_3^- slopes on Figure 5, a C/N ratio of 9±2 mol C mol N^{-1} for the organic material trapped in the shelf can be inferred. This number is in good agreement with the 7.82 reported by Olli, Wexels Riser, Wassmann, Ratkova, Arashekevich and Pasternak (this issue).

Figure 6 summarises the information in the previous paragraphs to produce a tentative partitioning of refractory, labile and semi–labile organic matter in waters upwelled–into and outwelled–from the shelf. The average TOC concentration at 500 m (~100% DOC) is 57 µM–C with a C/N molar ratio of 19±2. This depth level is just below the lower limit of ENACW off the NW Iberian Peninsula (Pérez, Mouriño, Fraga, & Ríos, 1993). The origin intercept of the regressions in Figures 5d (63 µM–C) and 5e (3.7 µM–N) can be considered as the mixture of refractory (90%, C/N~ 19±2) and semi–labile materials (10%, C/N ~9±2) transported by the shallower ENACW bodies which upwell over the shelf. A TOC excess of +14 µM–C, with a C/N molar ratio of 6.0±0.4, is observed in the study parcel of surface water outwelled to the adjacent ocean. It consists of labile materials, 50% POC and 50% DOC. Labile materials represents 18% of the organic carbon transported by the study volume. To produce this tentative partition we did three basic assumptions. **1**) DOM in oceanic ENACW is not going to undergo any transformation (biological or photochemical) during upwelling to the surface and subsequent outwelling to the adjacent ocean. Photochemical labilisation of coloured refractory DOM has been described when deep waters are promoted to surface UV–B natural levels (e.g.

Moran & Zepp, 1997). During an upwelling event, ENACW resides in the UV–B affected shelf surface layer (<20 m) ~5 days. Therefore, it is likely that we have underestimated the extension of the labile DOM fraction. **2**) the POM accumulated in the study water parcel can be considered as labile material. The slope of the direct correlation between POC_{susp} and PON_{susp}, 5.9±0.2 mol C^{-1} mol N^{-1}, supports this statement. The origin intercept, *i.e*. the fraction of POC_{susp} that does not covary with PON changes, only represents ~10% of the average POC_{susp} content in the study water parcel. **3**) The fractions of DOC and DON that covary with POC_{susp} and PON_{susp} (Figs. 5d and e) also contribute to the labile fraction. It should be noticed that the terms 'refractory', 'semi–labile' and 'labile' in Figure 6 are introduced to coin the three organic matter fractions with contrasting C/N molar ratios. Therefore, they just represent a relative rather than an absolute scale of reactivity.

3.2. The filament study

Hydrographic and chemical settings at the filament are quite distinct from the structure observed during the coastal upwelling study. A well–developed pycnocline at ~40m depth separates the warm (>16°C) and NO_3^- exhausted study water mass from the underlying cold and NO_3^- rich ENACW (Fig. 2). Shipboard NO_2^-+NO_3^- and NH_4^+ measurements in the nanomolar range confirms that N–nutrient is exhausted in the offshore–end of the filament (<7 nmol l^{-1} NO_2^-+ NO_3^-, <20 nmol l^{-1} NH_4^+). It is worth noting the brief (<0.15 µM–N) primary NO_2^- maximum observed below the pycnocline (Joint et al., this issue). DON and TON behave opposite to NO_3^-, with maximum concentrations in the surface mixed layer that decrease with depth to ~3.5 µM–N at 150m. There is no significant change in NO_3^- or TON (=PON_{susp}+DON) concentration between 14 and 17 August (Fig. 3a). After 14 August, DON increases (+0.5 µM–N) and PON_{susp} decreases (–0.4 µM–N) and from 15 to 17 August, DON consumption (–0.6 µM–N) accompanies PON_{susp} accumulation (+0.4 µM–N). Increases of POM_{susp} and decreases of DOM C/N ratios followed the initial conversion of PON_{susp} into DON (Fig. 4a). On the contrary, the POM C/N ratio decreases after 15 August while the DOM C/N ratio increases, which could be related with carbohydrates release (Norman et al., 1995; Søndergaard et al.,

2000). Therefore, the fresh organic matter produced at the inshore–start of the filament is still present off–shore. The evolution of NC_T and AOU (Fig. 3b) is also consistent with the NO_3^- one and no significant variations are measured from 14 to 17 August. Chlorophyll concentration in the off–shore filament (Fig. 4b) is ¼ of that at coastal upwelling study and the assemblage is dominated by smaller cells; 60% of the chlorophyll was in the <2µm fraction. Diatoms are absent and dinoflagellates dominate (77%) the biomass of microplankton species (Fig. 4c). It should be highlighted that microplankton counts are only representative for cell >5µm.

4. Discussion and Conclusions

Cold, nutrient–rich waters upwelled on the shelf of coastal upwelling systems may evolve to meso–scale cyclonic structures, 'upwelling centres', or occur as elongated plumes, 'filaments' (Traganza, Conrad & Braker, 1981). Our study in the NW Iberian upwelling system begins at the southern edge of the Cape Finisterre upwelling centre, where the water parcel is captured in an intermediate state of development after the spin–up phase of upwelling. At the eye of upwelling centres —characterised by high nutrients and low temperature and chlorophyll concentrations— reduced numbers of phytoplankton cells are promoted to the surface and have to adapt to the high light and nutrient conditions (e.g. MacIsaac, Dugdale, Barber, Blasco, & Packard, 1985; Dugdale & Wilkerson, 1989). Covariation between high NO_3^- and low temperature still persists at our intermediate state, although chlorophyll levels are relatively high, >0.5 mg m^{-3}. The initial C/N ratio of POM_{susp} (>8 mol C mol N^{-1}) suggests significant amounts of detritus, as has been observed in freshly upwelled waters off Point Conception, California (Jones et al., 1983). Subsequently, the study water mass evolves towards an advanced state of development where the thermal signal of the filament persists but nutrients become depleted. The time evolution of chlorophyll fractions during the inshore–start study indicates a succession to larger phytoplankton species, as confirmed by the progressive increase of diatoms. This is coherent with observations by Abbott et al. (1990) in the California upwelling system, who describe how the phytoplankton assemblage became progressively dominated by slow growing large centric diatoms as the drifter moved offshore. In fact, this is the time

development of a typical coastal upwelling system (Jones et al., 1983; MacIsaac et al., 1985; Dugdale & Wilkerson, 1989). On the contrary, during the offshore–end study NO_3^- is depleted in surface waters of the upwelling filament and reduced phytoplankton numbers concentrates at the deep chlorophyll maximum (DCM) being dominated by cells <2 μm. Microplankton biomass was almost exclusively composed by dinoflagellates and small flagellates, many of them heterotrophic. This is coherent with the dominance of small flagellates in warm, stratified and NO_3^- depleted oceanic waters (Cushing, 1989). Therefore, it seems that the food web in the study parcel of coastal water entrained by the filament undergo a transition from a coastal eutrophic to an offshore oligotrophic environment as suggested by Abbot et al. (1990).

Following Hood, Abbott, Hyer, and Kosro (1990), this contrasting patterns results primarily of the existence of two ecosystems separated by a strong front rather than a reflection of the temporal decline of phytoplankton biomass in parallel to increasing stratification of upwelled waters as they are exported offshore. In this sense, Wilkerson and Dugdale (1987) presented a 'conveyor belt' scheme where small species are selectively removed by the surface offshore flux of the 2–layer cross–shelf circulation and larger species are retained in the onshore flow and returned to the shelf. In addition, subduction of coastal waters entrained by the filament during offshore transport has been suggested by Brink and Cowles (1991) to explain the changes in surface nutrient concentrations and phytoplankton populations observed by Abbott et al. (1990). Floating drifters are constrained to remain at a constant near–surface depth in such a way that they will lost track of the original water parcel if subduction occurs. Subduction rates in the giant upwelling filament off Point Conception (California) ranges from 10 to 40 $m \cdot d^{-1}$ (Kadko, Washburn, & Jones, 1991) and affected the distribution of chlorophyll, phytoplankton and particle abundance (Jones, Morrers, Reinecker, Stanton & Washburn, 1991). Downwelling rates in the relatively small (65 km wide, 150 km long) filament off the 'Rías Baixas' are not comparable with those observed in the giant (200 km wide, 500 km long) filament off Point Conception. In addition, our drifter displaced in the middle of the offshore region of the filament and not along the northern edge where downwelling velocity is maximum

(Swenson, Niiler, Brink, & Abbott, 1992). Otherwise, we considered the time evolution of average changes from the surface to the 1%PAR or the nutricline (~50m), which integrates possible vertical displacements. In this sense, Moisan and Hofmann (1996) simulation of a lagrangian drifter entrained by an upwelling filament shows offshore subduction up to the level of the nutricline. This makes a difference with studies based on continuous records measured by a fixed depth drifter as it was advected offshore while entrained by the filament (Abbot et al., 1990). These considerations, together with the demonstration of the Lagrangian nature of the two drifter studies by Joint el al. (this issue), allow to assume that the time evolution of the chemical variables result from the NEM of the whole community of microorganisms in the study parcel of water.

4.1. Off–shelf export of primary production mediated through an upwelling filament

Net consumption of NO_3^- by the community of organisms in the study coastal water mass transforms into **1**) DON ($\varnothing<0.8\mu$) and PON_{susp} ($0.8\mu<\varnothing<200\mu$), which accumulates in the study volume, and **2**) PON_{sink} ($\varnothing> 200\mu$), which sinks off the study volume to shelf and slope sediments or it is actively transported by mesozooplankton. The time evolution of nitrogen species during the inshore–start study shows the expected chemical succession initiated with NO_3^- consumption, followed by PON_{susp} (phytoplankton) growth, and culminated with DON accumulation. The conspicuous evolution in C/N ratios of POM_{susp} and DOM also supports this view. Although this time segregation has been observed in cultures (e.g. Norrman, Zweifel, Hopkinson, & Fry, 1995), this is the first field observation. The conversion efficiency of NO_3^- consumption into TON accumulation during the transit of the study surface coastal waters from Cape Finisterre upwelling centre to the ocean is ~40%. Since the study water parcel crosses the shelf–edge (Fig. 1), this conversion efficiency is equivalent to a net ecosystem horizontal export ratio (e–ratio) of 0.4. The e–ratio reduces to 0.3 for the case of carbon, indicating that the shelf traps carbon more efficiently than nitrogen.

It is worth noting that DOC and DON represent about half of the organic carbon and nitrogen exported by the filament. The $-\Delta DOC/\Delta NC_T cor$ ratio is ~0.15 and the $-\Delta DON/\Delta NO_3^-$

ratio is ~0.20. These numbers agree very well with the 20% of ΔC_T assumed by Hansell and Carlson (1998) for the global coastal upwelling zone in their global estimates of DOC net community production. Although the key role of labile DOC and DON in the regenerated and new production of marine system is recognised nowadays (e.g. Bronk, Glibert & Ward, 1994; Hansell & Carlson, 1998), it has not been incorporated yet in the controversy about the fate of phytogenic materials in the coastal zone. Horizontal transport of recently produced POM_{susp} and DOM to the adjacent relatively barren offshore waters constitutes an alternative route for the export production from ocean margins, which has to be added to traditional sinks as sedimentation of POM_{sink} on shelf and slope. Filaments transporting organic materials produced in shelf waters hundreds of kilometres offshore into the ocean are recurrently observed in the major coastal upwelling regions of the World Ocean (e.g. Brink & Cowles, 1991; Gabric et al., 1993). If the e–ratios determined here for the NW Iberian Upwelling System can be applied to other filaments, the export fluxes have been dramatically underestimated because DOM was not included in budgets.

Average westward displacement of the water parcel during the offshore–end study is ~7 cm s^{-1}, half the velocities usually recorded in the giant upwelling filaments off California (Brink & Cowles, 1991). Velocities are larger in the offshore than in the onshore flowing portion in such a way that depth integrated (to 1% PAR) offshore POC_{susp} fluxes on the northern side of the filament are much greater than the onshore carbon flux to the south (Moisan et al., 1996). Considering **1**) the size of the offshore flowing section of the study water mass (~50m deep, ~32 km wide) and **2**) the labile/semi–labile POC_{susp}+DOC (20 μM–C) and chlorophyll (0.31 mg m^{-3}) concentrations, the study filament transports ~27 kg C s^{-1} and 35 g Chl s^{-1}. If this rough calculation is extrapolated to the period when the filament is active (May–September, ~150 days), ~3.5 10^8 kg C of labile POM_{susp}+DOM and 4.5 10^5 kg Chl are exported per year to the adjacent ocean. Since this filament is a major route for the export of primary production in shelf waters off the 'Rías Baixas' (3400 km^2), the resultant export per unit of shelf area is roughly 100 g C m^{-2} y^{-1}. This number represents as much as 45% of the annual primary production in the

study area, ~220 g C m^2 y^{-1} as estimated from Bode, Casas, Fernández, Marañon, Serret and Varela (1996) measurements. Our numbers are small compared with transport values obtained in the giant filaments off California (100–200 km wide, 100m deep), ranging from 170 to 506 g Chl s^{-1} (Jones et al, 1991; Strub, Kosro, Huyer and the CTZ collaborators, 1991; Moisan et al., 1996). Obviously, carbon export values are also small when compared with POC_{susp} fluxes of 158–1890 g C m^{-2} y^{-1} calculated by Moisan et al. (1996). If the 1/1 relative contribution of POC_{susp} and DOC to labile TOC exported by the study filament is extrapolable to other upwelling systems, previous calculations have probably underestimated the offshore flux of biogenic carbon by a half.

4.2. Lability of the exported materials

The exported pool consists of suspended particles (living phytoplankton & microheterotrophs, detritus) and dissolved materials that will serve as new sources for the growth and respiration of populations in the adjacent oceanic waters. The importance of DOM export for ecological functioning will depend on the lability of the transported materials and the trophic status of the region that receives that material. The community of heterotrophic bacteria living in the receptor ecosystem will rapidly use labile materials (Kirchmann et at., 1993). In addition, phytoplankton is able to use urea and some amino acids (Wafar, Le Corre & L'helguen, 1995). On the contrary, semi–labile materials will likely accumulate and will be eventually transported horizontally (Legendre & Le Fèvre, 1995) or vertically (Vidal, Duarte & Agustí, 1998). Accumulation of labile DOC has also been suggested when nutrient limitation occurs (oligotrophic systems) or when bacterial populations are controlled by microzooplankton grazing (Williams, 1995; Thingstad, Hagström & Rassoulzadegan, 1997). In addition, the conversion efficiency of labile DOC into bacterial biomass reduces from 30–50% in nutrient–rich to <5% in nutrient–limited systems (e.g. Fuhrman, 1992; Kirchman, Suzuki, Garside, & Ducklow, 1991; Hansell, Bates, & Gundersen, 1995). This has clear implications for the global carbon balance. If the exported DOC is included into higher trophic levels via the microbial loop, then it could be transferred to the deep ocean and would contribute to the temporary

sequestration of anthropogenic CO_2. If it is mineralised below 500m, it would be out of contact with the atmosphere for at least a few hundreds of years (Broecker & Peng, 1982).

In the case of the study filament, the question of the lability of the exported materials has been approached through the C/N ratio. The average composition of the initial products of phytoplankton production and early degradation (Anderson, 1995), $C_{106}H_{175}O_{42}N_{16}P$ (54.5% proteins, 25.5% carbohydrates, 16.1% lipids and 4.0% nucleic acids), has a molar C/N ratio of 6.6. The average C/N ratios of the POM_{susp}+DOM excess observed in the filament was 6.8±1.0 in the inshore–start and 6.5±0.4 in the offshore–end. Therefore, this has to be considered as a pool of labile materials. By contrast, the C/N ratio of the more refractory DOM in waters from 150 and 500m was respectively 17±1 and 19±2. The high nitrogen content of the exported materials makes it an attractive organic substrate for use by microbial populations in the adjacent oligotrophic ocean, but our study does not allow rising any conclusion regarding this point. Offshore export of labile POM_{susp}+DOM from upwelling systems must be considered in the controversy on the autotrophic (Williams, 1998) or heterotrophic (Del Giorgio, Cole & Cimbleris, 1997; Duarte & Agusti, 1998) status of oligotrophic surface waters. Assuming that 45% of the ~1 Gt $year^{-1}$ primary production in coastal upwelling systems worldwide (Wollast, 1998) is exported offshore, then 0.45 Gt C $year^{-1}$ of bioreactive organic matter would enter the food web of the oligotrophic ocean. This flux of new POC_{susp}+DOC represents >25% of the estimated export of semi–labile DOC from the surface to the deep ocean (assuming that it represents 30% of the total downward flux of organic carbon; Yamanaka & Tajika, 1997) and >10% of the global sinking flux in the open ocean (4.2 Gt C $year^{-1}$; Wollast, 1998). Recent observations by Bauer and Druffel (1998) indicate injection of old POC_{susp}+DOC from ocean margins directly into the deep ocean. Our work shows that ocean margins are also significant sources of recent materials to the surface ocean.

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the POM analyses, and P. Pazos (IIM) did the phytoplankton counts. The satellite image has been provided by the NERC RSDAS group at PML (CCMS), UK. Support for this work came from the EU project OMEX II – II (MAST3–CT97–0076) and the Spanish CICYT grant No. MAR97–1729–CE and MAR97–2068–CE.

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Figure captions

Figure 1. SST satellite image of the study area (Iberian upwelling system, SW Europe) showing the buoy track during the inshore–start (3–7 Aug 1998) and the offshore–end (14–17 Aug 1998) study of the upwelling filament south of Cape Finisterre. The symbols (Leg 1, circles, Leg 2, triangles) indicate the position of the buoy at the daily 02:00 GMT sampling site. The satellite image is from 12 August 1998, at mid–time of the experiment, and shows the SST imprint of the upwelling filament. The NERC RSDAS group at CCMS–PML (UK), has provided the image. Black lines are the –200 and –2000 m isobaths.

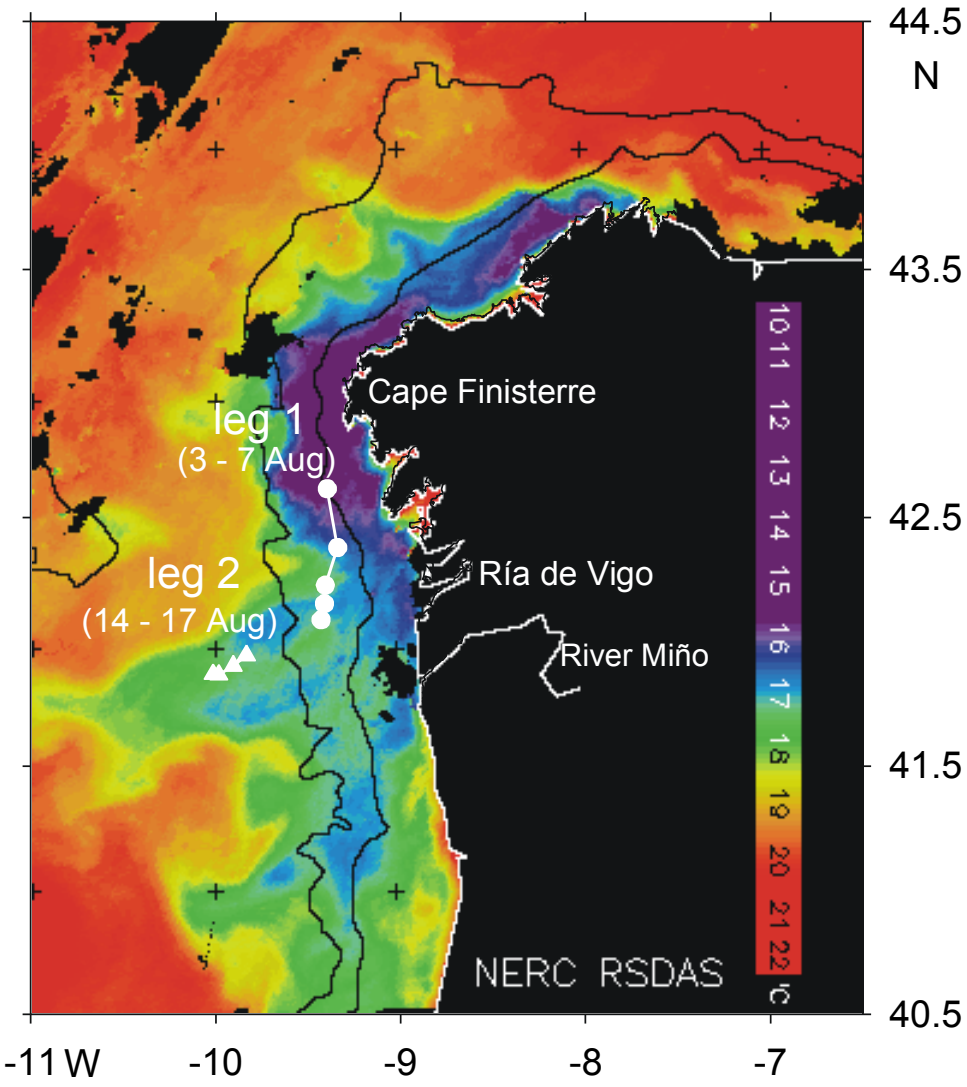
Figure 2. Time evolution of the 02:00 GMT temperature, nitrate (NO_3^-), dissolved organic nitrogen (DON) and total organic nitrogen (TON=PON_{susp}+DON) profiles during the inshore–start (**a)** and offshore–end study (**b**) of the filament. Shaded areas indicate the study water volume, with the 1% photosynthetic available radiation (PAR) defining the lower limit of depth.

Figure 3. Time evolution of (**a**) the average concentrations of NO_3^-, PON_{susp} & DON–3.7 (µM–N); and (**b**) $CaCO_3$–corrected total inorganic carbon (NC_T, µM–C) & apparent oxygen utilisation (AOU= O_2–O_2saturation, µM–O_2) in the study water mass during the inshore–start and offshore–end study of the filament. Figure 3a includes the total distance covered by the drifting buoy. DON–3.7 represents the DON excess compared with DON levels in upwelled ENACW (3.7 µM–N).

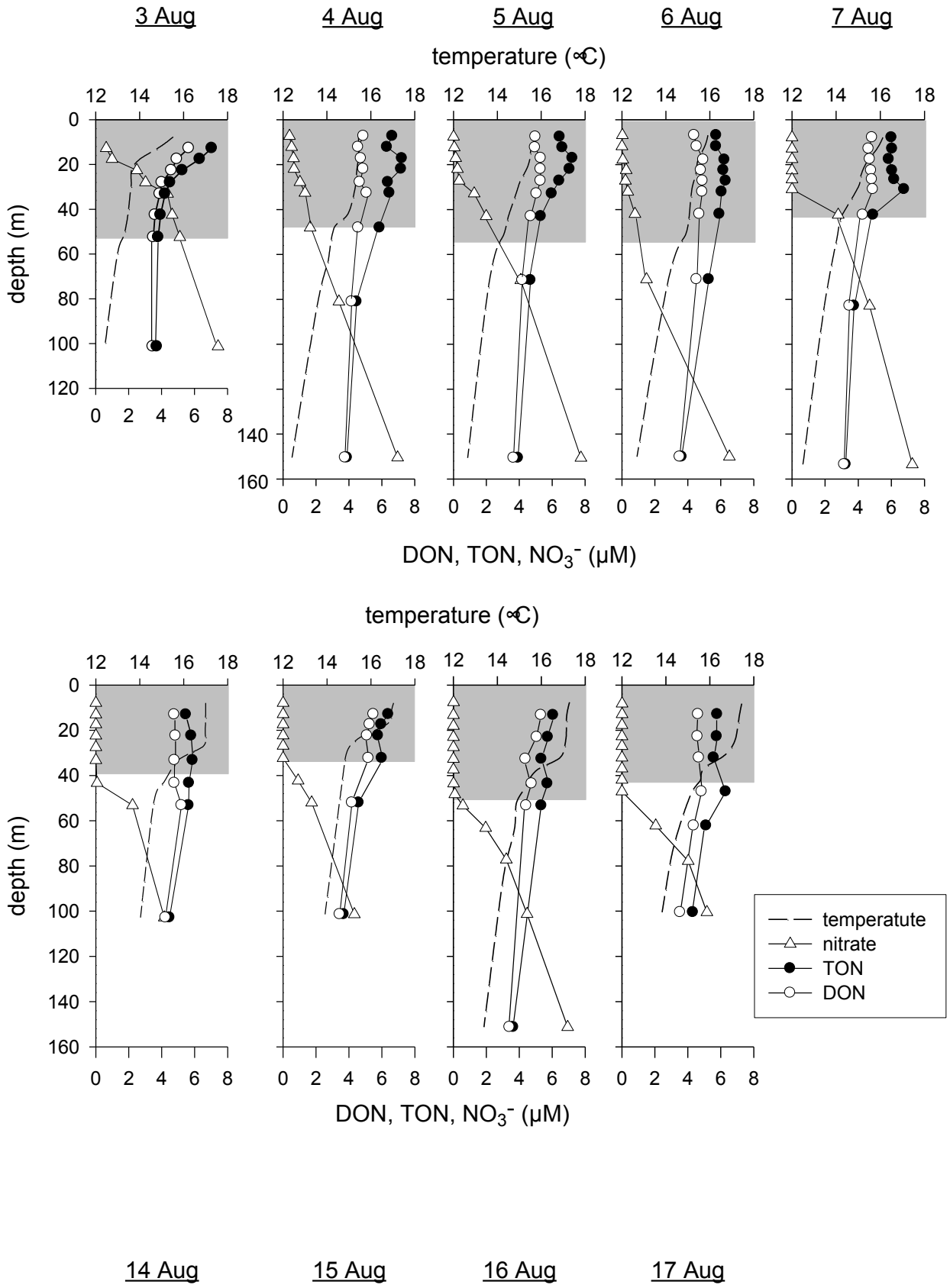
Figure 4. Time evolution of (**a**) the average C/N molar ratio of the suspended (POM_{susp}) dissolved (DOM) & total (TOM) organic matter; (**b**) chlorophyll concentration (mg m^{-3}) of three size fractions (<2 µm, 2–5 µm, >5 µm); and (**c**) the percentage of diatoms, dinoflagellates, ciliates and others (referred to total microplankton carbon) in the study water mass during the inshore–start and the offshore–end study of the filament. Small flagellates and cryptophycea (small cells) mainly compose the group of 'others'.

Figure 5. X–Y plots and linear regression equations (model II; Sokal and Rohlf, 1995) for NC_Tcor *versus* NO_3^- (**a**), TOC *versus* TON (**b**), POC_{susp} *versus* PON_{susp} (**c**), TOC *versus* POC_{susp} (**d**) TON *versus* PON_{susp} (**e**) and TON *versus* NO_3^- (**f**) for all bottle data during the inshore–start study of the filament (3–7 August 1998).

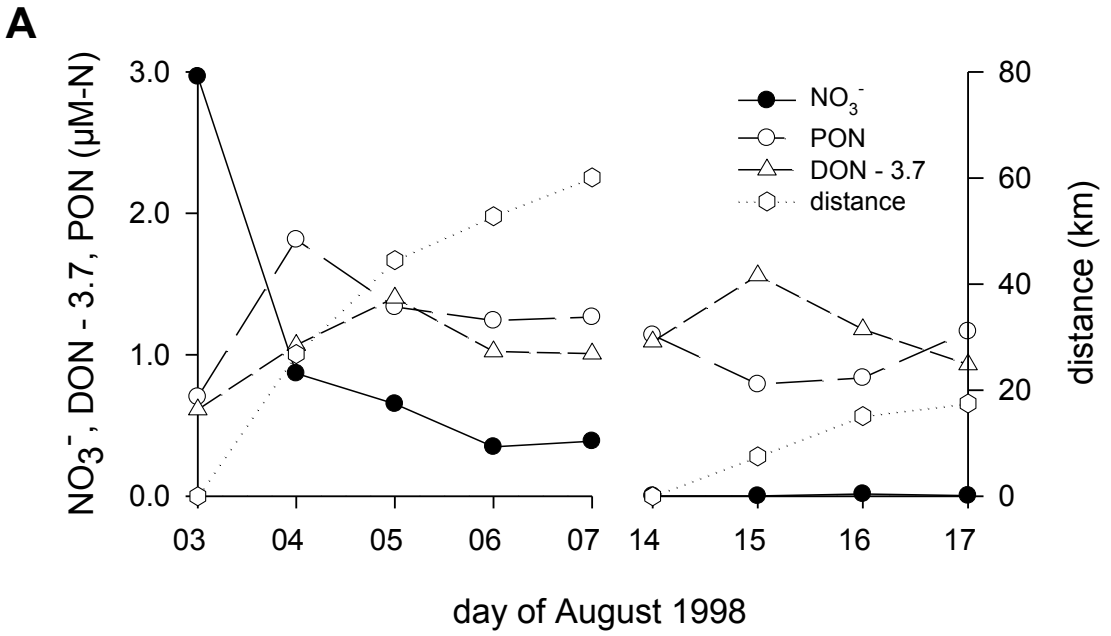
Figure 6. Tentative partitioning of refractory, semi–labile and labile organic carbon transported by the upwelled ENACW and the outwelled study volume of surface waters during the inshore–start study of the filament (3–7 August 1998). Concentrations in μM–C.



Alvarez–Salgado et al., Figure 1



Alvarez-Salgado et al., Figure 2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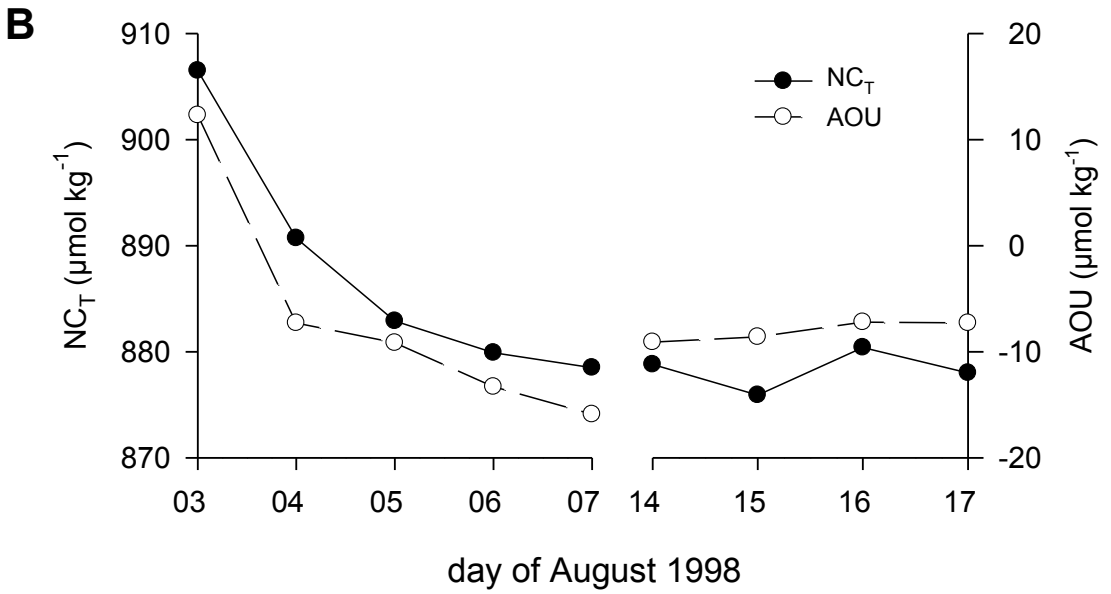
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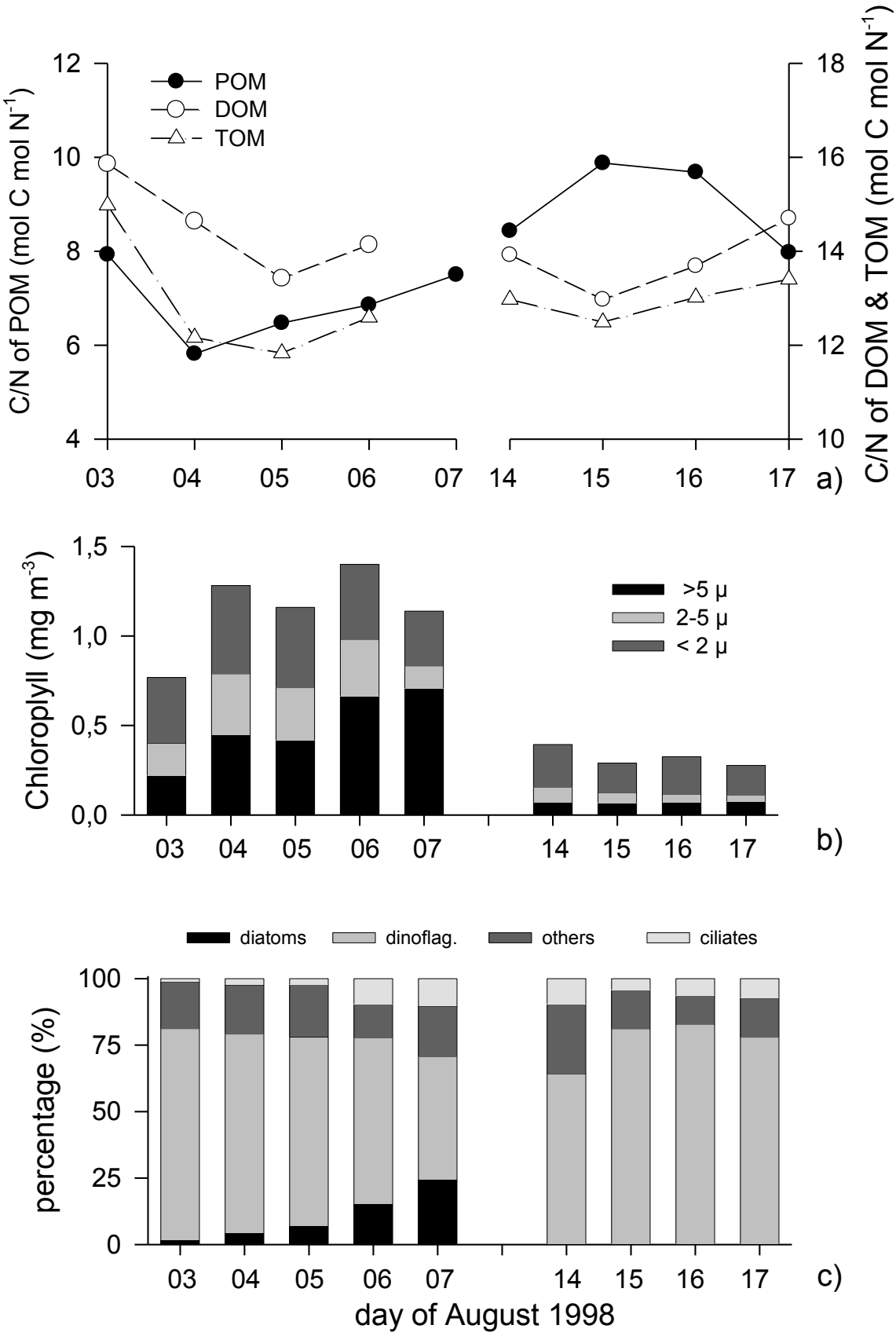
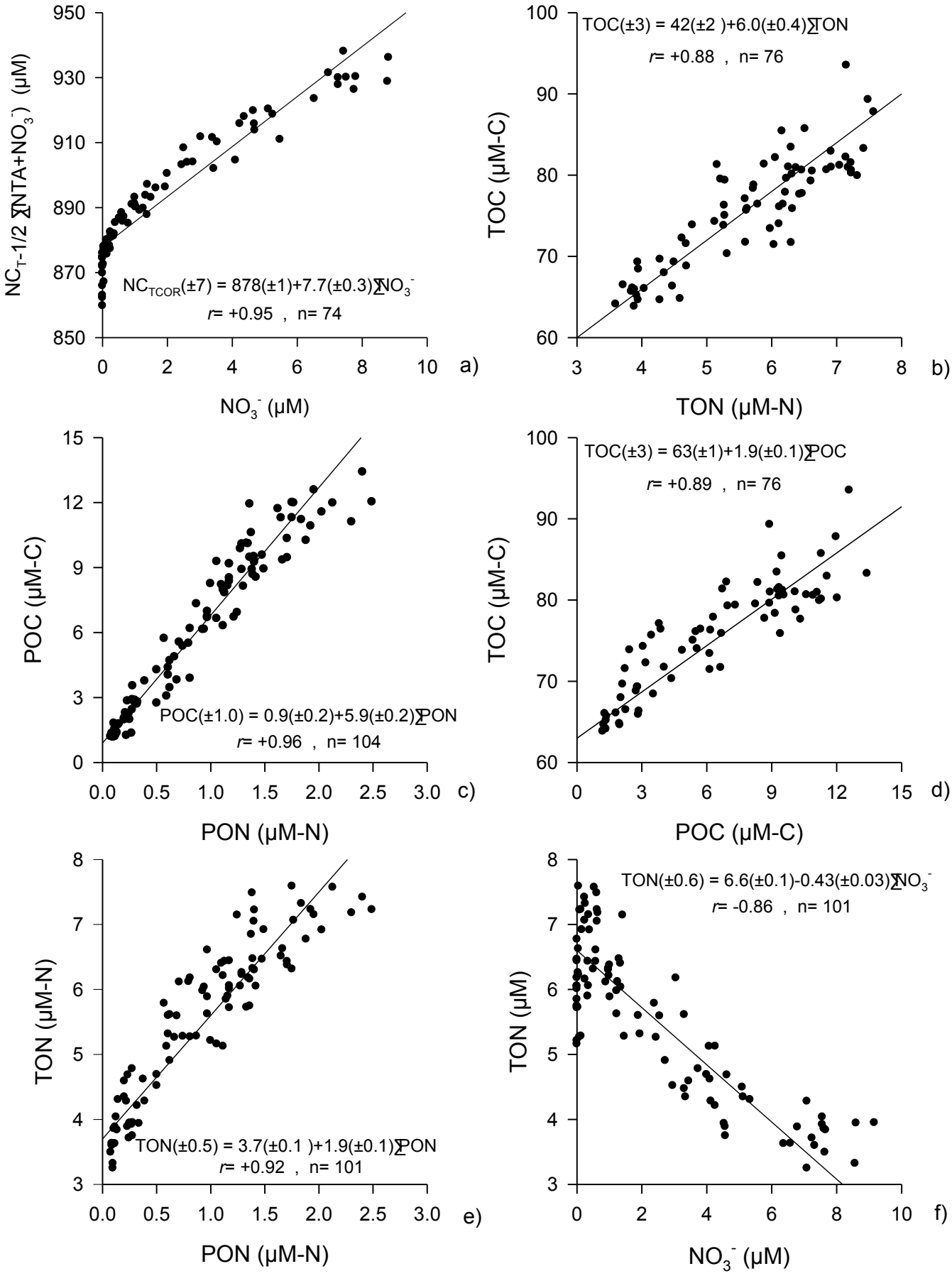
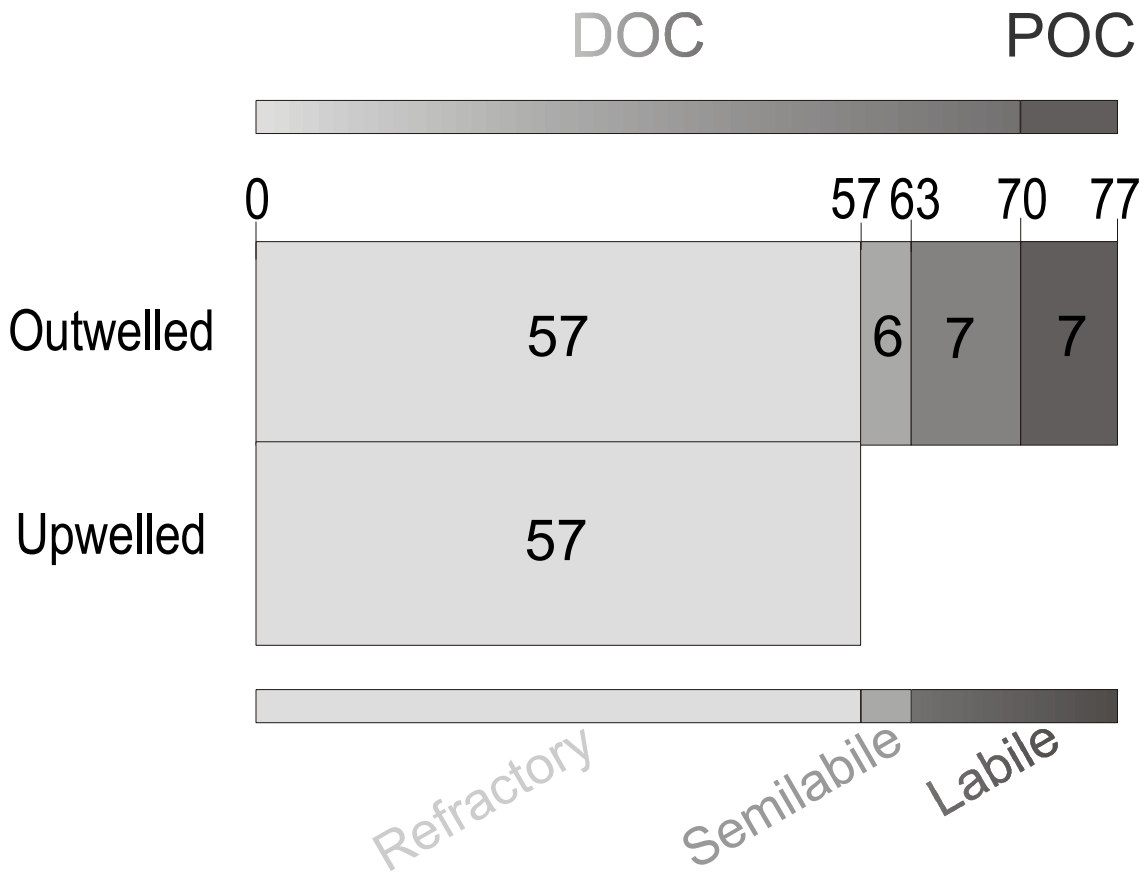
880
870
NC_T (µmol kg^{-1})
20
10
0
-10
-20
AOU (µmol kg^{-1})
NC_T
AOU
03
04
05
06
07
14
15
16
17
day of August 1998



Alvarez-Salgado et al., Figure 4



Alvarez-Salgado et al., Figure 5



Alvarez–Salgado et al. Figure 6